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Differences between LaB_6 and CeB_6 by means of spectroscopic ellipsometry

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Abstract. The optical properties of LaB_6 and CeB_6 have been investigated using spectroscopic ellipsometry. The results were compared with band-structure calculations. The main features of the spectra of both materials originate from optical transitions starting at boron-derived levels of similar character. A sharp peak in the joint density of states for CeB_6 around 0.5 eV is observed.

1. Introduction

The hexaborides have received considerable attention over the years both from an industrial and from a pure scientific point of view. LaB_6 is a refractory compound with a low workfunction. It is very suitable as an electron beam source which can be used at relatively low temperatures and which possesses a high brightness. CeB_6 has similar properties.

Moreover, it is intriguing to investigate the behaviour of the 4f electron. We summarise some of the properties specific to CeB_6 . At high temperatures, T larger than about 50 K, and low fields one observes a Curie–Weiss law behaviour of the magnetic susceptibility; an effective moment is obtained, being slightly lower than the moment of a free Ce^{3+} ion, 2.32 compared with $2.54 \mu\text{B}$. At low temperatures and low fields the material orders antiferromagnetically, $T_N = 2 \text{ K}$ in zero field is obtained. The magnetic moment, found with neutron diffraction, is $\sim 0.65 \mu\text{B}$ (Horn *et al* 1981). As a function of applied field an interesting set of magnetic phases is observed at low temperatures; we refer to the work by Kasuya (1983). Steglich (1985) determined the linear term in the specific heat at $T \simeq 0.1 \text{ K}$ to be large and strongly dependent on a magnetic field. One infers a strong variation of the electronic contribution to the specific heat when a field is applied.

In order to investigate the electronic properties of materials, LaB_6 has been investigated by means of several surface sensitive techniques: UPS (Aono *et al* 1979), XPS (Nishitani 1980). Also De Haas–Van Alphen measurements were performed on LaB_6 and CeB_6 (Arko *et al* 1976, van Deursen *et al* 1982; van Deursen and de Vroomen 1985). Band-structure calculations exist for LaB_6 (Hasegawa and Yanase 1977, Arko *et al* 1976) and for CeB_6 (Yanase 1983). Ellipsometry measurements were performed on CeB_6 and

LaB₆ in order to investigate any differences between the compounds spectroscopically. The experimental data obtained in ellipsometry experiments give information about the band structure several eV below and above E_F . Ellipsometry is an especially good method for complex materials, which are more difficult to study in photoemission experiments, e.g. (van der Heide 1984, 1985a, b). For LaB₆ optical properties were determined by several authors using reflectivity measurements (Kierzek-Pecold 1969, Gurin 1980, Shelykh 1981). These results are less reliable, as they need Kramers–Kronig relations to calculate the dielectric constants.

2. Method

2.1. Experiment

For the measurements a spectroscopic ellipsometer was used, with a range from 0.5–6.0 eV. The equipment has been described elsewhere (van der Heide 1984). From the experimental data the dielectric constants ϵ_1 and ϵ_2 are calculated directly. Also other quantities such as reflectivity, optical conductivity and skin depth can be obtained. For a comparison with band-structure calculations the joint density of states (JDOS) and the optical conductivity σ are the most important quantities. When one assumes constant matrix elements for the optical transitions, one has

$$\text{JDOS} = A \sum_{i,f} \int d\mathbf{k} \delta(E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar\omega) = \omega^2 \epsilon_2$$

$$\sigma = \omega \epsilon_2$$

where i and f denote the initial and final states involved. As CeB₆ and LaB₆ have a cubic crystal structure the dielectric constants can be calculated using the formulae for isotropic samples (Born and Wolf 1959). However, it is by no means certain that the approximation of constant matrix elements is valid in the case where 4f states are involved.

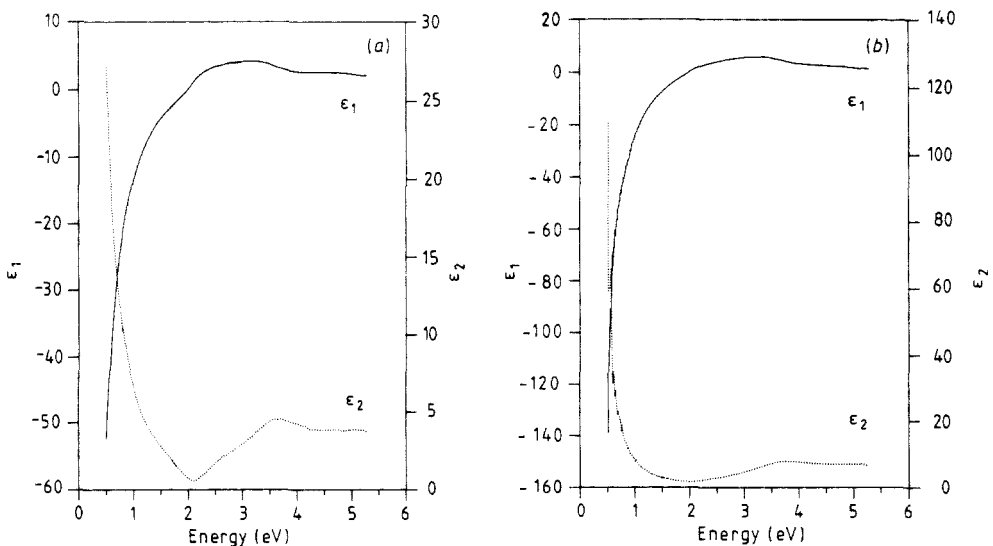


Figure 1. The dielectric constants ϵ_1 and ϵ_2 of LaB₆ (a) and CeB₆ (b).

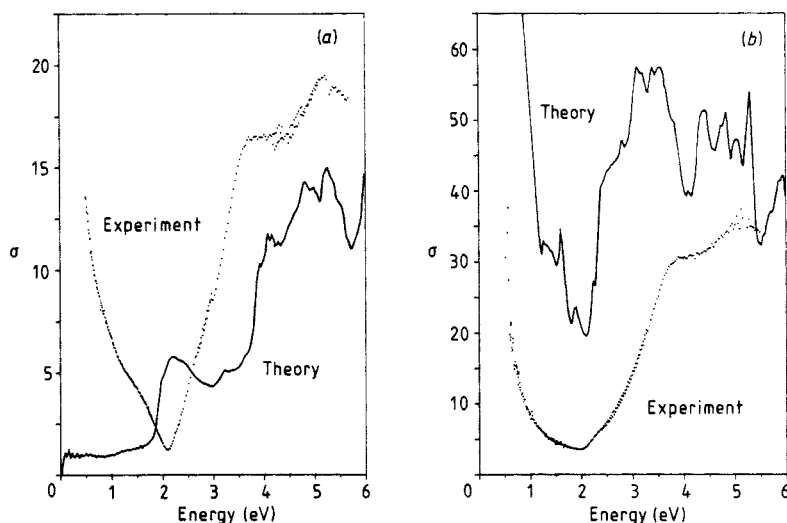


Figure 2. Optical conductivity of LaB_6 (a) and CeB_6 (b).

The samples used were single crystals with a diameter of 4 mm and the surface normal along the (100) axis. The samples were polished using diamond powder down to $1\ \mu\text{m}$. Immediately after polishing the samples were introduced into the vacuum system.

The values of ϵ_1 and ϵ_2 for LaB_6 and CeB_6 are given in figures 1(a) and (b) respectively. The errors in the measured values are a few per cent, as was deduced from measurements on Ni_3Al (van der Heide *et al* 1985b). The optical conductivities of LaB_6 and CeB_6 are given in figure 2(a) and (b). These spectra look very similar. The experimental optical conductivities contain both an intraband (Drude) contribution, which is only important at energies below 1 eV, and an interband absorption contribution which dominates at higher energies. The main features of the LaB_6 spectrum are a broad shoulder extending from

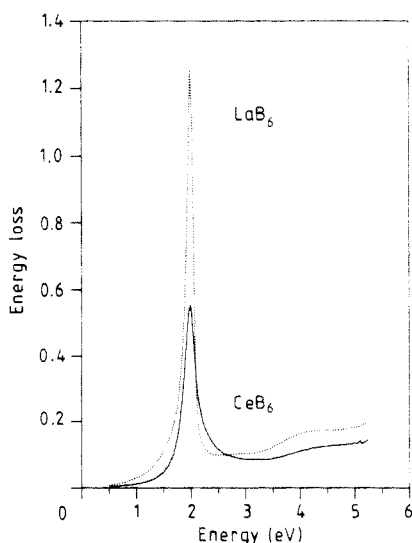


Figure 3. Energy-loss function of LaB_6 and CeB_6 .

1.25 to 2.0 eV with a maximum at 1.6 eV and strong absorption bands extending from 3.7 to 4.25 eV. CeB₆ has a similar spectrum with a broad shoulder extending from 2.0 to 2.6 eV centred at 2.3 eV. There are also strong absorption bands visible from 3.65 to 4.40 eV. For CeB₆ a very steep decline of the optical conductivity in the infrared region is also observed at 0.5 eV.

A dominant feature of the optical properties of rare-earth hexaborides is the existence of plasmons. These plasmons are most clearly seen in the energy loss function; which is given by $\text{Im}(1/\epsilon) = \epsilon_2/\epsilon_1^2 + \epsilon_2^2$. The energy loss functions for LaB₆ and CeB₆ are displayed in figure 3. It is seen that both plasmon peaks have an identical energy position but different peak heights and widths. They are well defined because ϵ_2 is small when $\epsilon_1 = 0$, especially for LaB₆. The plasma frequencies ω_p and scattering times τ corresponding to these peaks were calculated assuming a Lorentzian line profile (Raether 1980). Both materials have a plasmon at $\hbar\omega_p = 2.0$ eV. LaB₆ has a scattering time of 4.3×10^{-15} s and CeB₆ a scattering time of 2.3×10^{-15} s. The scattering times thus differ by approximately a factor of two.

3. Theory

The band structure of LaB₆ and CeB₆ was calculated using the ASW method (Williams *et al* 1979). The basis set was composed of s, p, d and f wavefunctions and boron s and p functions. Boron 3d functions were treated perturbatively, but were not included in the Hamiltonian.

The resultant secular matrix was of rank 40 and the calculations required eight iterations to obtain convergence to an accuracy of $1:10^{-5}$. The band structures along the lines of high symmetry of the simple cubic Brillouin zone were plotted in figure 4 and figure 5 for LaB₆ and CeB₆ respectively. The band-structure calculations were performed without spin polarisation for both LaB₆ and CeB₆. It is usually better to compare a magnetic system (CeB₆) above its ordering temperature with a calculation of the ordered magnetic

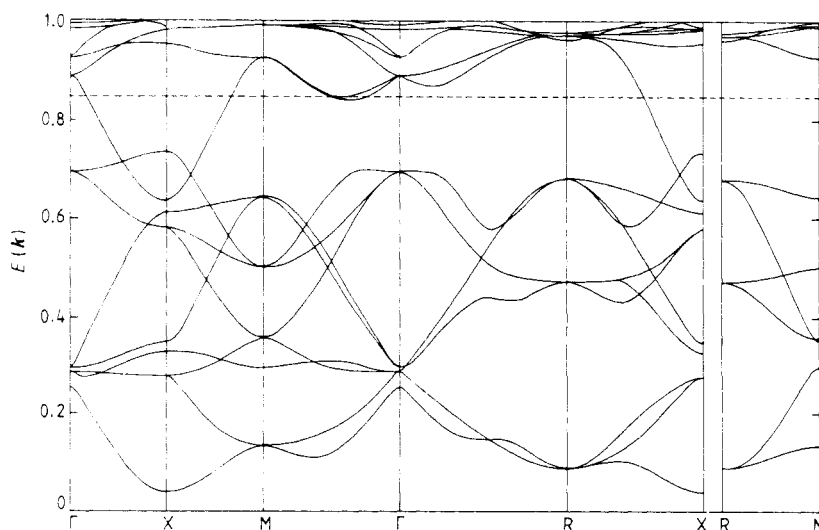


Figure 4. Band structure of LaB₆ along high symmetry lines.

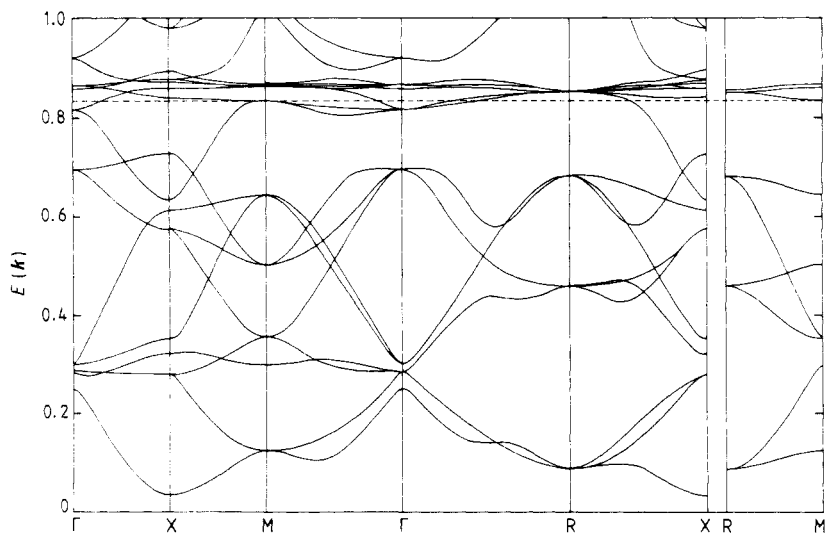


Figure 5. Band structure of CeB_6 along high symmetry lines.

state rather than the non-magnetic state. This is because a calculation without spin polarisation does not correspond to the paramagnetic state but to a hypothetical diamagnetic state, comparable with the paramagnetic state in the limit of high temperatures. Since the measurements reported here were performed at room temperature ($\sim 150 T_N$) we prefer the non-magnetic calculation here. The differences between the calculated non-magnetic and calculated hypothetical ferromagnetic state were small however (at most 0.1 eV).

The results for LaB_6 are in very close agreement with the results of Hasegawa and Yanase (1977) but deviate from those of Arko *et al* (1976). The bandstructure of CeB_6 is in good agreement with the bandstructure calculated by Yanase (1983). The band structures obtained for LaB_6 and CeB_6 show great similarities. The lower nine bands are of primarily B character, although the hybridisation with the metal d states at the top of the complex is substantial. In LaB_6 the Fermi level is positioned in a band complex of mixed B-p, La-d character. At Γ , one finds a doublet of La d E_G symmetry and finally the La 4f complex is reached at about 1 Ryd. The higher states in CeB_6 deviate from this picture, as expected. Above the lowest nine bands one finds a complex of 7f bands, hybridised with B p as well. The doublet at Γ at the highest energy is of Ce E_G d character. The joint density of states was calculated for the two materials using the quadratic integration scheme of Methfessel *et al* (1983). The optical conductivity calculated from the JDOS is shown in figures 2(a) and (b) for LaB_6 and CeB_6 respectively.

4. Discussion

From the comparison of the optical conductivities calculated from the band structure and the experimentally determined optical conductivities, the nature of the transitions involved can be deduced: in LaB_6 the shoulder at 1.6 eV corresponding with the theoretical peak at 2.2 eV, stems from transitions at the top of the boron p complex to the empty La d levels. The experimental feature at 4.0 eV originates from the same initial states, it corresponds

with the theoretical feature which starts at 4 eV. The role of the final states is here performed by the higher-lying empty f levels of lanthanum.

Both of the features in CeB₆ find their origin in transitions towards empty Ce f levels, the shoulder at 2.3 eV is formed by transitions from the top of the boron p complex; the feature at 4.0 eV is caused by transitions from lower-lying B p states.

For neither materials could a reliable Drude fit be made. This is also in agreement with the band-structure as for these materials interband transitions have already set in at the low energies of 0.1 eV. The sharp decline of the optical conductivity for CeB₆ at 0.5 eV can be interpreted by a peak in the JDOS at the same energy. The peak is due to transitions from the occupied bands to the unoccupied bands of the f complex around the Fermi energy. These bands are hybridised with d levels.

The plasmons observed are also common to other hexaborides: EuB₆, PrB₆ and NdB₆ (Kierzek-Pecold 1969, Gurin *et al* 1980). For all these materials they occur at exactly the same energy. From the band-structures described it can be seen that interband transitions start at very low energies, which probably leads to a shift in the free electron value of the plasmon energy to 2.0 eV.

To summarise, we conclude that CeB₆ and LaB₆ have similar optical properties. An additional structure at 0.5 eV in CeB₆ is guessed from the more rapid increase of $\sigma(\omega)$, indicating transitions in the hybridised f level complex at the Fermi energy.

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